PB 188 082

AIR POLLUTION ASPECTS OF AMMONIA

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Bethesda, Maryland

September 1969

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AIR POLLUTION ASPECTS

OF

AMMONIA

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
Department of Health, Education, and Welfare

Compiled by Sydney Miner

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September 1969

FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Ammonia is a natural constituent of the atmosphere but exists in concentrations below the level which is hazardous to humans, animals, plants, or materials. High concentrations of ammonia gas are corrosive to mucous membranes; can cause damage to the eye, throat, and upper respiratory tract; and can produce residual damage and even death in humans and animals. High concentrations are also toxic to most plant life and have corrosive effects on materials.

Almost all of the ammonia in the atmosphere is produced by natural biological processes, largely from the decomposition of organic waste material. Man contributes a comparatively small portion of ammonia to the atmosphere, mainly through combustion and industrial processes involved in the production or use of ammonia.

Air quality standards for ammonia concentrations have not been established in the United States. Measurements of environmental concentrations indicate average levels of approximately 20 $\mu g/m^3$.

Wet scrubbers, bag filters, and charcoal filters are used to control industrial losses of ammonia to the atmosphere. The economic value of ammonia encourages its conservation in commercial processes. No economic data are available on damages caused by ammonia pollution.

Adequate methods are available for the detection and measurement of ammonia in the atmosphere.

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1. INTRODUCTION

The main source of atmospheric ammonia is naturally-produced ammonia which is released from land and ocean areas. In terms of total air content of ammonia, urban-produced ammonia is of lesser importance, though it may be important from the air pollution standpoint in localized situations.

The primary source of ammonia air pollution in cities is the combustion process involved in the combustion of fuels, incineration of wastes, and use of the internal combustion engine. Industrial sources emitting ammonia are chemical plants, coke ovens, and refineries. Other sources are stock-yards and similar installations, where ammonia is formed by biological degradation.

2. EFFECTS

2.1 Effects on Humans

Ammonia gas, if inhaled, affects mainly the upper respiratory tract, according to Jacobs.[30] Only a small percentage of an inhaled dose reaches the lungs at the inhaled concentration. At high concentrations (1,700,000 $\mu g/m^3$ to 4,500,000 $\mu g/m^3$), ammonia acts as an asphyxiant. At concentrations of 280,000 $\mu g/m^3$ to 490,000 $\mu g/m^3$ the gas can produce eye, nose, and throat irritation.

Silverman et al.[62] exposed seven adult males to ammonia gas concentrations of 350,000 $\mu g/m^3$. Significant effects on respiration resulted, as well as irritations of the throat and nose and hypoesthesia.

Kustou[37] ran 7-to-8-hour tests to determine the effect of ammonia on certain physiological and biological indexes in man. He found that at concentrations of 13,000 $\mu g/m^3$ the urea and ammonia content of the blood and the urine increased. In addition, he noted a lowering of the oxygen use factor and some respiratory depression.

In 1955 Hemeon[24] suggested that zinc ammonium sulfate aerosols were in part responsible for the irritant effects of the air during the Donora Smog Episode in 1948. Amdur and Corn[4] found that aerosols of zinc sulfate, zinc ammonium sulfate, and ammonium sulfate produced severe irritation in guinea pigs. The double salt was the most irritative. They established that the smaller the particles, the greater the

irritative action and that the aerosols, in conjunction with sulfur dioxide gas, produced synergistic effects. This synergistic effect was particularly enhanced when the ammonium sulfate and zinc ammonium sulfate were combined with sulfur dioxide gas.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No reports were found on effects of ammonia on livestock, although they can be expected to be negligible at the low concentration normally found in urban or rural atmospheres. High localized concentrations due to accidental releases of ammonia could cause significant effects.

2.2.2 Experimental Animals

Several studies have been made on the effects on experimental animals both of ammonia alone and of ammonia and carbon combinations. Weedon[76] reported that guinea pigs and rabbits exposed to 1,740,000 $\mu g/m^3$ of ammonia developed acute and chronic lung lesions. The rabbits were less sensitive than the guinea pigs, which tolerated around 1,000,000 $\mu g/m^3$. When Weedon[76] exposed house flies to ammonia concentrations of 700,000 $\mu g/m^3$, 6 percent of the flies were killed in 16 hours. He also exposed mice and rats to 700,000 $\mu g/m^3$ of ammonia for 16 hours. Two older animals showed some evidence of slight dyspnea. At the end of the exposure, the eyes of all the rats and mice were bright, with little or no evidence of lacrimation. The gross findings at autopsy for one rat

(considered typical of the exposed group), which died 12 hours after exposure are shown in Table 1.

TABLE 1

GROSS FINDINGS AT AUTOPSY
OF RAT EXPOSED TO 700,000 $\mu g/m^3$ AMMONIA[76]

Organs	Findings (Rat which died 12 hr. after exposure)
Brain	Slightly congested
Trachea	Not reddened
Lungs	Two-thirds distended, many large hemorrhages, cherry-red, waxy, cut surface foamy
Heart	Much distended
Liver	Congested
Gall bladder	Not distended
Stomach	Moderately distended, few hemorrhages
Intestines	Large intestine partly distended
Adrenals	Pink
Kidneys	Congested
Peritoneal surfaces	Not remarkable

Weatherby[74] exposed guinea pigs to 118,000 $\mu g/m^3$ of ammonia and found mild changes in kidneys, spleen, adrenals, and liver in 18 weeks. No change was found in 12 weeks. J. Dalhamn[13] found that low concentrations of ammonia (2,000 $\mu g/m^3$) caused the cilia of the upper respiratory tract of rats to stop beating in 8 to 9 minutes. Friberg[20] found that the process of arresting the cilia was reversible until concentrations around 210,000 $\mu g/m^3$ of inhaled air were reached.

T. Dalhamn and L. Reid[14] exposed rats to 70,000 $\mu g/m^3$ of ammonia and 7,000 $\mu g/m^3$ of pulverized carbon in air for 6 months. The severe mucosal damage and impairment of ciliary activity observed suggested a synergistic effect.

2.3 Effects on Plants

Thornton[71] exposed tomato plants, buckwheat, and tobacco plants to air concentrations of ammonia of 700; 2,800; 1,000; 44,000; 175,000; and 700,000 $\mu g/m^3$ in air for periods of 1, 4, 15, 60, and 240 minutes. He found that ammonia at 700,000 $\mu g/m^3$ caused changes in the pH of tomato plant leaf and stem tissue but did not cause damage at lower concentrations. He also found that there was some correlation between pH change and observed injury. The time required to produce injury to 50 percent of the exposed plant surfaces at 700,000 $\mu g/m^3$ is shown in Table 2. In general, acute injury due to ammonia is shown by a collapse of tissue without subsequent loss of chlorophyll. Definite injury was observed on buckwheat, coleus, sunflower, and tomato after exposure to 38,000 $\mu g/m^3$ of ammonia for about 1 hour; slight injury was observed at 11,500 $\mu g/m^3$ after 4 hours; and at 5,600 $\mu g/m^3$, the plants were either uninjured or slightly marked after 5 hours. Nearly all parts of the leaf had a cooked green appearance which became brown upon drying.[17,64,69-71]

Treshaw[73] indicated that ammonia can induce glazing and silvering, particularly of lower leaf surfaces of vegetables.

TABLE 2

TIME IN MINUTES UNTIL 50% INJURY TO EXPOSED PLANT SURFACES AT 700,000 $\mu g/m^3$ [71]

Part of Plant	Plant	Time (min)
Leaves	Tomato	3
	Buckwheat	5
	Tobacco	8
Stems	Tomato	60
	Buckwheat	30
	Tobacco	240

Benedict and Breen[9] fumigated 10 species of common weeds which occur throughout the United States in an effort to develop a method for identifying pollutants causing damage. The ammonia produced spots of cell collapse and death, primarily along the margins of the leaves. With grasses, small spots developed over the area where the leaf bends, giving a powdery appearance. The powdery marking increased in the region between the bend and the tip as the intensity of fumigation was increased. Table 3 shows the percentage of leaf area marked by ammonia at concentrations of 8,400 $\mu g/m^3$ and 2,100 $\mu g/m^3$. Table 4 shows the relative sensitivity of the weeds to ammonia.

Barton[8] exposed radish seeds and spring rye seed to 700,000 $\mu g/m^3$ and 175,000 $\mu g/m^3$ of ammonia in air. Both dry and soaked seeds were used in each case. The germination of soaked radish seeds exposed for as long as 240 minutes to 700,000 $\mu g/m^3$ of this gas was not only delayed but actually

TABLE 3

PERCENTAGE OF LEAF AREA MARKED BY AMMONIA[9]
(Four-hour fumigations)

Plant	Concentration of Ammonia 8,400 µg/m³			2,100 µg/m³		
	3 wk[a] Moist[b]	6 wk[a] Moist[b]	6 wk[a] Dry[b]	3 wk[a] Moist[b]	6 wk[a] Moist[b]	6 wk[a] Dry[b]
Mustard	33	48	8	15	10	8
Sunflower	32	32	2	4	2	2
Lamb's-quarters	5	20	11	2	2	1
Cheeseweed	5	19	3	1	1	1
Annual bluegrass	6	11	1	2	1	1
Kentucky bluegrass	4	13	1	0	0	0
Dandelion	3	8	2	0	0	0
Chickweed	1	9	1	0	0	0
Pigweed	2	4	2	1	2	1
Nettle-leaf goosefoot	1	1	1	0	0	0

[a]Age of plants.
[b]Soil condition.

TABLE 4

RELATIVE SENSITIVITY OF WEEDS TO AMMONIA[9]

Sensitive	Intermediate	Resistant
Mustard	Lamb's-quarters	Dandelion
Sunflower	Cheeseweed	Chickweed
	Annual bluegrass	Pigweed
	Kentucky bluegrass	Nettle-leaf Goosefoot

reduced. An extension of the treatment period to 960 minutes killed all of the seeds. A 1-minute exposure had no retarding effect. The germination of seeds treated in the dry state was delayed by 240 minutes' exposure.

Rye seeds were more sensitive to ammonia than those of radish. Exposures of soaked seeds to 700,000 $\mu g/m^3$ for as long as 240 minutes resulted in 100-percent kill, while those exposed to 175,000 $\mu g/m^3$ for 960 minutes had a germination rate of only 48 percent.

Classes of organisms differ in their sensitivity to ammonia gas. Leaves are the most sensitive, followed by stems, fungi, and bacteria, which are intermediately sensitive. Seeds are least sensitive of all to the gas.[44]

2.4 Effects on Materials

Ammonia associated with sulfur dioxide and moisture can cause crystalline bloom defects on the surface of varnish and paints, according to Holbrow.[25] In another study, Preston[57] exposed various metallic surfaces to fine powders in atmospheres of varying humidities. The character of the resulting corrosion was filiform, typical of highly reactive particles in the atmosphere. Ammonia can also discolor some fabric dyes.[1]

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists at their 29th Annual Meeting in 1967 recommended an occupational threshold limit for ammonia in air of 35,000 $\mu g/m^3$. The Bureau of Medicine and Surgery, Department of the

Navy, has recommended an ammonia threshold limit for 1 hour of 280,000 $\mu g/m^3$.[75] The permissible limit for ammonia in a submarine during a 60-day dive is around 18,000 $\mu g/m^3$.[75] No ambient air quality standards for ammonia exist for the United States. However, such ambient air standards exist for Czechoslovakia, the U.S.S.R., and Ontario, Canada, as shown in Table 5.

TABLE 5

AMBIENT AIR QUALITY STANDARDS FOR AMMONIA[66]

	Basic Standard[a]		Permissible[b]	
Location	$\mu g/m^3$	Averaging Time	$\mu g/m^3$	Averaging Time
Czechoslovakia	100	24 hr	300	30 min
U.S.S.R.	200	24 hr	200	20 min
Ontario, Canada	3,500	30 min		

[a] Basic standard for long-term exposure.
[b] Permissible standard not to be exceeded more than once in any 4 hours.

3. SOURCES

The major portion of atmospheric ammonia is produced by biological processes in land and sea masses, and the gas then escapes into the atmosphere.[59] Ammonia produced by industry and as a result of urban activities, though of lesser importance, may nevertheless be a factor in air pollution in localized areas. The major source of urban-produced ammonia is the combustion process which occurs in operation of the internal combustion engine, combustion of fuels for heating, and the incineration of wastes. Industrial sources of ammonia are refineries, fertilizer plants, and organic chemical process plants. Other minor sources of ammonia arise from biological degradation in areas where animals are kept, such as stockyards, and from miscellaneous uses of ammonia in cleaning both in industry and in the home.

3.1 Natural Occurrence

According to Frost and Sullivan,[21] 3.7×10^9 tons of ammonia are released into the atmosphere annually. Of this amount, only 4.2×10^6 tons are emitted to the atmosphere as a result of industrial and urban processes; therefore, roughly 99.9 percent of the atmosphere's ammonia concentration is produced by natural biological processes. Jung[32] indicates that the main biological source of ammonia is the decomposition of organic waste material. Approximately 1.0 g of ammonia per man per day is produced metabolically.[35] Ammonia is given off from manure in piggeries[15] and other installations where

animals are kept. Ammonia is also generated during treatment of waste water in sewage plants.[39] No information was found on the quantity of these emissions. Ammonia is also found in sea water and in volcanic gases.

3.2 Production Sources

Ammonia is produced commercially in chemical process plants, as a by-product in the manufacture of other chemicals, mainly in making coke from coal, and as a product of combustion, refining of oils, and other processes.

3.2.1 Haber-Bosch Process

The Haber-Bosch process for the production of ammonia accounts for over 85 percent of the total commercial yield. This process involves the combining of hydrogen and nitrogen gases in the presence of a catalyst. The hydrogen is usually obtained from water gas (a mixture of carbon monoxide and hydrogen), and the nitrogen is obtained from the air. Hydrogen and nitrogen are combined with the catalyst in the ammonia generator to form ammonia when heated to temperatures of 450 to 600°C under pressure of 200-1,000 atmospheres.

The world's production of ammonia in 1965 was 26.8 million tons, and this is expected to reach 70 million tons by 1970.[77] In the U.S.A., 7.8 million tons of ammonia were produced in 1964. By 1968 this had increased to 17.25 million tons.[68] The 1968 ammonia production rates by States are shown in Table 6.

In 1962, there were 64 synthetic ammonia plants in this country, while in 1964 there were 95. By 1966 this number had increased to 109.[77]

TABLE 6

AMMONIA PRODUCTION IN 1968[68]

State	Thousand Short Tons/Yr
Texas	3,150
Louisiana	3,150
California	1,300
Mississippi	1,250
Arkansas	850
Iowa	800
Pennsylvania	625
Nebraska	600
Illinois	525
Ohio	450
All Other States	4,550
Total	17,250

3.2.2 Coke Plants

In a report on Russian coke ovens, Kapitulskii[34] states that the usual ammonia concentration in air samples at the top of a coke oven during charging was 6,300 to 8,000 $\mu g/m^3$. This was reduced to 3,500 to 4,400 $\mu g/m^3$ by smokeless charging--that is, diverting the coke-oven gas by vacuum to the gas-collection main. No data were found on ammonia emissions from coke-oven plants in the United States.

In 1966 about 66 million tons of coke were produced per year in this country in 66 coke-oven plants. The value of the coke at the coke oven was estimated to be $1,144 million. The production rate of coke from 1957 to 1968 is shown in Table 7.

TABLE 7

U.S. COKE PRODUCTION[47]

Year	Tons/Year	No. of Oven Slots
1957-1959	60.5×10^6	15,993
1964	60.9×10^6	14,639
1965	65.2×10^6	14,357
1966	66.0×10^6	14,720

3.2.3 Oil Refineries

The main source of ammonia in oil refineries is from the catalyst regenerators in the catalytic cracking plants. The ammonia releases from oil refineries are given in Table 8.

TABLE 8

AMMONIA RELEASED FROM OIL REFINERIES[6]

Source	Lb/100 Bl of Fresh Feed
Compressor-Internal Combustion	0.2
Fluid-Bed Catalytic Cracking Units	54.0
Thermofor Catalytic Cracking Units	5.0

Table 9 gives the ammonia emissions from regenerator stacks in catalytic cracking units of the Los Angeles area refineries.[6]

At the time the data were compiled, there were 18 refineries in the Los Angeles area with a combined capacity of 700,000 barrels of crude oil per day.

TABLE 9

AMMONIA EMISSION FROM CATALYTIC CRACKING UNIT REGENERATOR STACKS[6]
(Los Angeles Refineries)

Unit Type	$\mu g/m^3$	Tons/Day
Fluid bed	47,000-470,000	4.2
Thermofor	20,000-72,000	0.2

In 1960 there were approximately 300 oil refineries distributed throughout the U.S.A. The catalytic cracking capacity of these refineries was 3.7 million barrels per day of fresh feed plus 1.1 million barrels per day of recycle.[6] By 1968 there were around 270 refineries in the U.S.A., with a catalytic cracking capacity of 4.1 million barrels per day of fresh feed and 1.6 million barrels per day of recycle.[22,67] The total catalytic cracking capacity from 1960 as projected to 1969 is shown in Figure 1. The cracking charge capacity and the States in which the units were located in January 1968, are shown in Table 13 in the Appendix.

3.2.4 Metallurgical and Ceramic Plants

Typical exhaust emissions[28] from some metallurgical and ceramic plants are as follows:

From nonferrous foundries: per plant producing 50 tons of castings per day — 0.002 tons of ammonia

From gray iron foundries: per plant producing 200 tons of castings per day — 0.023 tons of ammonia

From stone, clay, and glass plants: per cement plant producing 4,830 barrels per day — 0.17 manufacturing tons

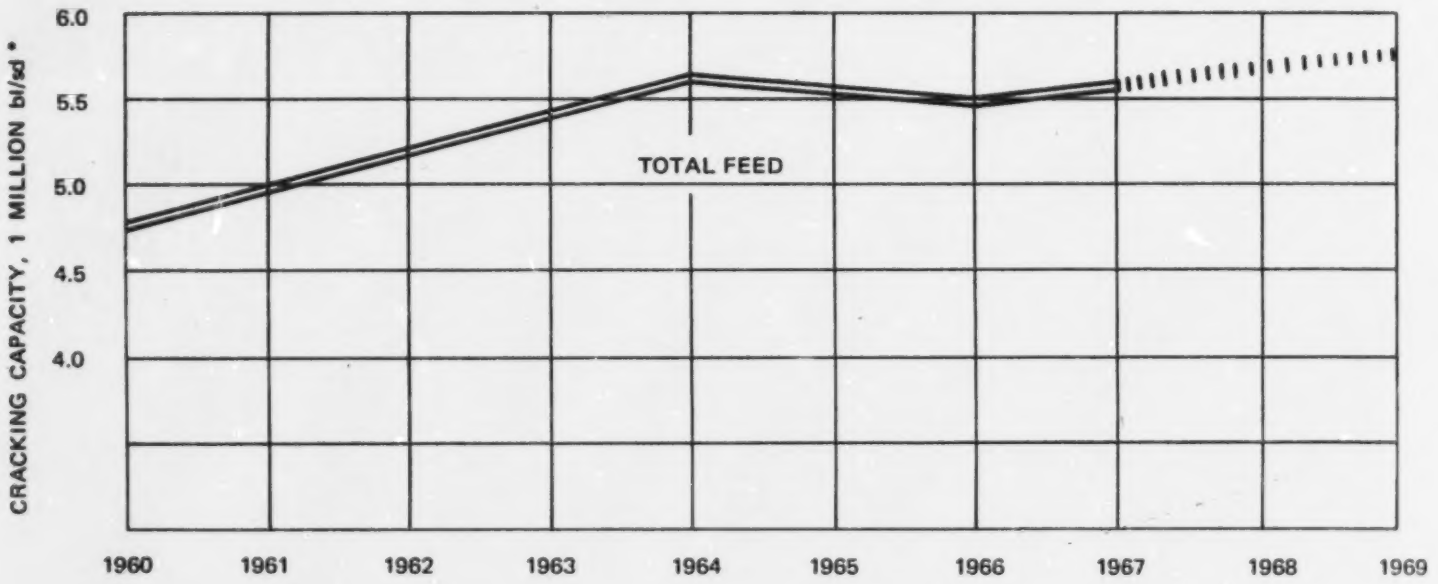

FIGURE 1

Total Catalytic Cracking Capacity of Oil Refineries[61]

3.2.5 Combustion Processes

Ammonia is produced as a result of combustion, mainly from the use of fossil fuels and incineration of waste materials. These sources generally result in direct emission of the ammonia into the atmosphere.

The emission of ammonia from internal combustion engines has been estimated at 2.0 lb/1,000 gallons burned for gasoline engines[11,26,43] and for diesel engines.[26] The total ammonia emitted daily into the atmosphere of Los Angeles from the combustion of gasoline in 1953 was estimated at 5.0 tons a day. The rates of emissions of ammonia from various categories of fossil fuels is presented in Table 10.

TABLE 10

AMMONIA EMISSIONS FROM COMBUSTION[11,26,59]

Combustion Source	Amount of Emission
Coal	2 lb/ton
Fuel oil	1 lb/1,000 gal
Natural gas	0.3 - 0.56 lb/10^6 ft^3
Bottled gas (butane)	1.7 lb/10^6 ft^3
Propane	1.3 lb/10^6 ft^3
Wood	2.4 lb/ton
Forest fires	0.3 lb/ton

The amounts of ammonia discharged daily from domestic heating sources using each fuel in a metropolitan area of 100,000 persons are given in Table 11.

TABLE 11

POUNDS OF AMMONIA DISCHARGED DAILY IN METROPOLITAN AREA OF 100,000 PERSONS USING EACH HEATING SYSTEM

Domestic Heating Fuel	Total Pounds
Coal	2,000
Oil	800
Gas	0.3

In 1967 the total consumption of fossil fuel in the U.S.A. comprised almost 5 million barrels of oil, around 19 trillion cubic feet of natural gas, and 550 tons of coal.[18] The trends of fossil-fuel consumptions in the utility industry alone are shown in Figure 2.

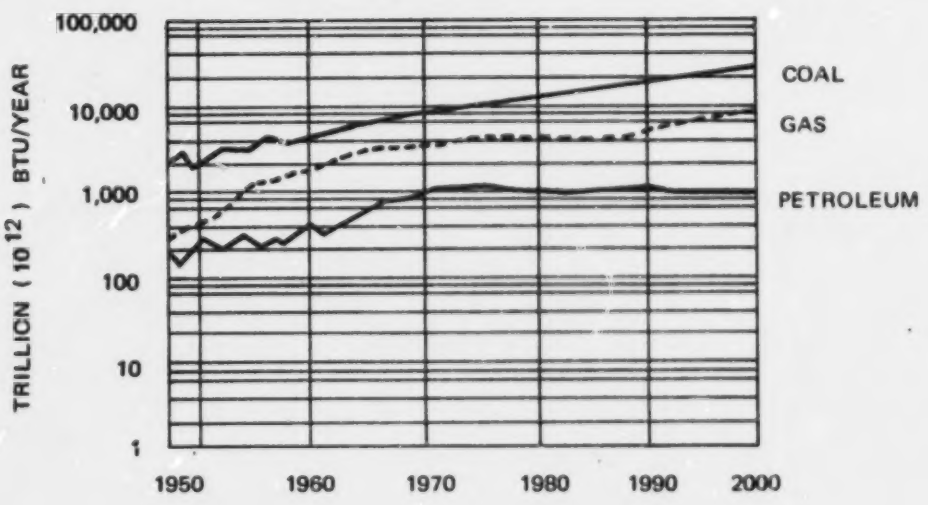

FIGURE 2

Trends in Electric Utility Fossil Fuel Consumption[18]

The demand in the United States for gasoline topped 5 million barrels per day in 1968 and is expected to reach 5.5 million barrels per day in 1969. The trend in gasoline demand between 1959 and 1968 is shown in Figure 3.

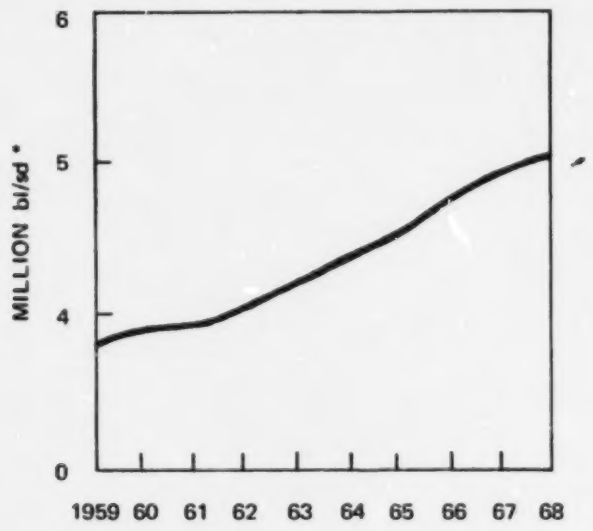

FIGURE 3

Motor Gasoline Demand[19]

The emission of ammonia from incineration of solid wastes is shown in Table 14 in the Appendix. The total ammonia emitted from domestic and industrial solid waste disposal that might be expected from a metropolitan area of 100,000 population, using several methods of disposal, is shown in Table 15 in the Appendix.

The United States produces at the present time about 170 million tons of refuse per year, of which about 15 percent is incinerated. In 1980, about 260 million tons per year of refuse will be produced, and the percentage to be incinerated is expected to increase about 50 percent. The

expenditure for incinerators in 1966 was 50 million dollars. This figure is expected to rise to 100 million dollars by 1980.[21]

3.3 Product Sources

Ammonia is used as a raw material in the production of nitric acid, fertilizers, and the syntheses of hundreds of organic compounds, including many drugs, plastics, and dyes. Approximately 85 percent of the ammonia is used as anhydrous ammonia fertilizer or as a raw material for other fertilizer production.

Very little information is available on ammonia emissions from these plants. It has been reported that 2,600 tons of ammonia per year are released from a fertilizer plant in South Point, Ohio.[28] Another reference reported that 0.078 tons of ammonia are released for each plant consuming 109 BTU/day in the chemical and allied products industry.[58]

Burakhovitch made air pollution surveys in the vicinities of chemical plant complexes in Russia. The plants involved produced mineral fertilizers, synthetic monomers, ammonia alcohols, plastics, and nitric acid. Sampling sites were situated at 2,000 and 4,000 meters from the principal discharge sources. The ammonia concentrations measured showed a significant reduction of ammonia pollution between 1963 and 1964, attributable to the construction of waste-gas absorbers in the nitric acid plant and improvement in ammonia manufacturing technology by the changeover to natural gas.

In dilute solutions ammonia is used domestically, commercially, and industrially as a cleansing agent. Ammonia is also used in developing drawing reproductions. Table 12 shows the emissions of ammonia when used for cleaning machinery and developing reproductions of drawings.

TABLE 12

MISCELLANEOUS AMMONIA EMISSIONS[58]

	$\mu g/m^3$	Remarks
Manufacturing of machinery-cleaning with ammonia	10,500	Sporadic task (one time=8 hours per week)
Developing plans and reproductions with ammonia	5,600	Sporadic

Little information was found on the ammonia concentration in the air in the home. Holbrow[25] observed that the ammonia concentration inside houses in England may rise to several times that in the outside air and may even approach that of sulfur dioxide.

3.4 Environmental Air Concentrations

The average concentration of ammonium compounds in the air in urban areas is approximately 20 $\mu g/m^3$.[38,42,60] The background concentration of ammonium in the lower troposphere is about 6 $\mu g/m^3$ in the mid-latitudes and 140 $\mu g/m^3$ near the equator.[59] Data on atmospheric concentrations of ammonium for various cities of the United States are presented in Tables 16 and 17 in the Appendix.

4. ABATEMENT

No information has been found on the abatement of ammonia as such in air pollution; however, methods used to abate other pollutants with which it is associated also reduce the quantity of ammonia that reaches the atmosphere. For example, in smokeless charging of coke ovens (that is, collecting the bulk of escaping coke-oven gas, coal dust, and tar by vacuum during coke-oven charging), the ammonia emissions to the atmosphere are cut in half.[34]

In incineration systems where wet scrubbers are used to remove fly ash, the ammonia in the gas stream leaving the incinerator should also be reduced. However, no information was found on this subject.

In the chemical industry, where ammonia is used as a raw material, its recovery is a matter of fundamental economic importance; methods have therefore been designed to minimize its loss. For high concentrations of ammonia, gas wet scrubbers can be used. For ammonia concentrations in air between approximately 16 to 27 percent (flammable range)[56] the gas can be flared. Impregnated activated charcoal has been used to remove ammonia from the air in laboratories that use animals in research and in other places where animals are kept in large numbers.[40] Where the ammonia occurs as a solid--as ammonium sulfate in the fertilizer industry for instance--conventional methods for solids removal can be used such as bag filters, electrostatic precipitators, and wet scrubbers.

5. ECONOMICS

In the future, greater emissions of ammonia to the atmosphere may be expected as a result of increases in incineration, fuel oil usage, catalytic cracking, and gasoline consumption. These added emissions should be offset by the growing number of improved abatement systems installed principally to reduce emission of other substances, such as particulates, hydrocarbons, and sulfur dioxide. However, no information has been found on the effectiveness of these systems in removing ammonia, or on the number of abatement systems to be installed.

The economic impact of ammonia pollution on humans, plants, and animals is expected to be minimal since at normal atmospheric concentrations the ammonia will have little or no deleterious effect. Localized accidental emissions of ammonia in high concentrations could have serious economic impact resulting from death or sickness of animals or humans and damage to plants. No information has been found on the economic costs of ammonia air pollution or on the costs of its abatement.

Data on production and consumption of ammonia are presented in Section 3.

6. METHODS OF ANALYSIS

The primary method used in air pollution for analyzing for ammonia in air is the Nessler colorimetric method.[10,42,65] The sample is collected by passing the air through a standard impinger containing 0.1N sulfuric acid. The collected sample is then contacted with Nessler's reagent and examined in a colorimeter. If a cloudy solution forms after the addition of Nessler's reagent, alkaline Rochelle salt is added to clear it up.[29]

To obtain more accurate results prior to Nesslerization, the acidic sample may be made alkaline and the ammonia distilled into a receiver containing .02N sulfuric acid.[7] Nessler's reagent is then added, and the sample is analyzed colorimetrically. The Nessler colorimetric method of analysis gives the total ammonia content of the air: i.e., both gaseous and particulate components. Equipment based on Nessler's method has been developed for automatic analysis.[2]

Another method utilized for analyzing for ammonia is the indophenol blue technique. The sample is collected as outlined above. It is then contacted with alkaline phenol and sodium hypochlorite, which turns it blue-green. The sample color is then read on a colorimeter. The ammonia determined is the total ammonia and ammonium in the sample. This method was developed for controlled atmosphere applications but can be applied to air pollution work. The indophenol blue technique has also been adapted for use in automatic ammonia analyzers.[35]

Smolczyk[63] showed that paper impregnated with phenolphthalein will change color in air in the presence of 10 to 100 ppm (7,000-70,000 $\mu g/m^3$) of ammonia gas. Kuramoto[36] used impregnated diazotized alpha or beta-naphthylamine to test for ammonia.

Cambi[10] indicated that ammonia samples with as little as 0.01 ppm (7 $\mu g/m^3$) ammonia can be analyzed by titrating directly with standard solutions of sodium hydroxide and sulfuric acid. In addition, industrial methods based on infrared analysis and colorimetric techniques[42] are used for ammonia analysis.

7. SUMMARY AND CONCLUSIONS

Atmospheric concentrations of ammonia are generally below the level at which health hazards and deleterious effects to humans, animals, plants, and materials are known to occur. High concentrations, usually caused by accidental spillage, can result in corrosive action to mucous membranes, permanent injury to the cornea, damage to the throat and upper respiratory tract, chronic bronchial catarrh, and edema. In sufficiently high doses (1,700,000 $\mu g/m^3$-4,500,000 $\mu g/m^3$), ammonia acts as an asphyxiant. Ammonia combines with sulfur oxides and metallic materials in the atmosphere to form ammonium sulfate and zinc ammonium sulfate aerosols. These aerosols are thought to be in part responsible for the irritant effects of the air during the Donora Smog Episode in 1948. Severe irritation was produced by these salts in guinea pigs.

Ammonia has been shown to be toxic to most plant life, producing injury to leaf and stem tissue, and reducing or delaying germination of seeds at concentrations of 700,000 $\mu g/m^3$. It also has a corrosive effect on certain materials.

The bulk of the ammonia found throughout the world in the atmosphere is produced by natural biological processes which release this substance to the air. The background concentration of ammonium is 6 $\mu g/m^3$ in the mid-latitudes and 140 $\mu g/m^3$ near the equator. A secondary source of atmospheric ammonia is urban-produced ammonia, which may be

an important source in localized situations. The average concentration of ammonium in the urban atmosphere is 20 $\mu g/m^3$, although measurements as high as 7,200 $\mu g/m^3$ have been recorded in areas adjacent to chemical manufacturing complexes.

The combustion process, the main source of urban-produced ammonia in the atmosphere, includes combustion of fuels, incineration of wastes, and use of the internal combustion engine. Industrial sources consist of chemical plants, coke ovens, and refineries. Ammonia air pollution also results from biological degradation in piggeries, stockyards, and similar installations.

Equipment such as wet scrubbers, and bag filters added to control systems to reduce other combustion-product emissions will also reduce ammonia emissions. In coke ovens, ammonia emission can be reduced along with other gases and dust by collecting the coke-oven gases during charging and discharging. In chemical plants, ammonia emissions are generally kept to a minimum due to economic considerations; however, wet scrubbers can be used to reduce emissions even more effectively. In places where animals are kept, impregnated charcoal has been used effectively to control ammonia pollution.

The economic impact of ammonia pollution on humans, animals, plants, and materials is believed to be minimal, due to the low natural concentrations of ammonia and the absence of harmful effects at these levels. Data on economic losses from ammonia are not available. Localized accidental emissions

could, of course, create loss of life and serious damage to plants. No information has been found on the cost of abatement of ammonia air pollution.

The ammonia concentration in the atmosphere can be measured manually or automatically by the Nessler or indophenol blue technique.

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APPENDIX

APPENDIX

TABLE 13

CATALYTIC CRACKING CAPACITY OF OIL REFINERIES IN U.S.A.[68]
(January 1968)

State	Barrels per day Fresh Feed	Recycle
Arkansas	28,500	10,200
California	431,800	173,570
Colorado	15,500	8,500
Delaware	62,000	44,000
Hawaii	13,000	
Illinois	287,780	108,315
Indiana	211,700	70,900
Kansas	139,550	82,250
Kentucky	47,500	5,500
Louisiana	472,710	133,845
Michigan	54,000	31,150
Minnesota	40,000	14,500
Mississippi	55,500	33,500
Missouri	36,000	18,000
Montana	40,800	36,900
New Jersey	245,445	93,780
New Mexico	11,200	7,000
New York	33,000	9,000
North Dakota	20,500	10,300
Ohio	182,200	91,800
Oklahoma	178,650	84,025
Pennsylvania	229,200	79,460
Tennessee	11,000	4,000
Texas	1,138,065	356,965
Utah	42,200	19,250
Virginia	25,000	15,000
Washington	80,775	30,600
Wisconsin	5,000	5,000
Wyoming	42,025	16,610
Total	4,180,600	1,599,120

APPENDIX

TABLE 14

AMMONIA EMISSIONS FROM INCINERATION [18,24,25,27,59]

Combustion Source	$\mu g/m^3$	lb/ton of material burned
Gas-fired domestic incinerators		
shredded paper and domestic wastes	<4,000	
Older units		
shredded paper	4,000	
Municipal incinerators		
spray chamber (Alhambra, Calif.)	20,000	0.3
multiple chamber		0.4
Other incinerators		
Single chamber	400	0.3-0.5
Wood waste	800	
Backyard paper and trimmings	45,000	1.8
Backyard 6 ft^3 paper	3,000	0.1
Backyard 6 ft^3 trimmings	100,000	4.4
Open dump burning		2.3
Large gas-fired industrial units	400	
Flue-fed apartment incinerators		0.4

APPENDIX

TABLE 15

POUNDS OF AMMONIA DISCHARGED DAILY FROM INCINERATION IN A METROPOLITAN AREA OF 100,000 PERSONS[22]

Source	Total Pounds
Domestic disposal	
Backyard burning	345
Apartment incinerator	24
Municipal disposal	
Incineration	45
Burning dumps	345
Sanitary land fill	Trace

TABLE 16

U.S: NATIONAL AMMONIUM CONCENTRATION [40,41,42]

Location	Year	Measurements	
		Average $\mu g/m^3$	Maximum $\mu g/m^3$
National Average (National Air Surveillance Measurements)	1964-65	1	75
New York City	1955-57	20	260
	1955-60	30	110
	1955-62	20	70

APPENDIX

TABLE 17

CONCENTRATIONS OF AMMONIUM IN AIR, UNITED STATES[42]

Location	Year	No. of Samp.	Micrograms Per Cubic Meter												Std Geom Dev
			Min	Frequency Distribution-Percent									Max	Arith Mean	Geom Mean	
				10	20	30	40	50	60	70	80	90				
Alabama																
Mobile	1964	26	.1		.1	.1	.2	.2	.3	.4	.9	1.5	2.2	.5	.3	2.74
Alaska																
Anchorage	1964	24	.1			.1	.1	.1	.1	.2	.2	.3	.4	.2	.2	1.59
Arizona																
Phoenix	1964	25	.1		.1	.1	.1	.2	.2	.3	1.3	3.9	4.7	.8	.3	3.64
Tucson	1964	25	.1		.1	.1	.1	.2	.2	.2	.3	.6	2.0	.3	.2	2.18
Arkansas																
Little Rock	1964	25	.2	.2	.4	.5	.5	.6	.8	1.0	1.1	1.3	2.8	.8	.7	1.95
California																
Bakersfield	1964	25	.2	.3	.4	.7	.7	.8	1.4	2.0	2.4	5.4	13.5	2.0	1.1	2.79
Burbank	1964	24	.2	.3	.6	.9	1.8	2.1	3.1	3.7	4.6	7.5	10.5	3.0	1.9	3.01
Los Angeles	1963	25	.1	.1	.2	.2	.3	.4	.5	.9	1.5	2.9	8.9	1.1	.5	3.16
Oakland	1964	25	.2	.2	.2	.3	.3	.3	.3	.4	.4	.9	5.4	.7	.4	2.16
Pasadena	1964	26	.2	.4	.6	.7	1.3	1.8	3.2	3.9	5.4	6.1	17.9	3.3	1.8	3.20
Sacramento	1964	26	.1	.1	.1	.2	.2	.3	.4	.5	.8	1.1	2.5	.5	.4	2.34
San Diego	1964	25	.1	.1	.1	.2	.2	.3	.3	.4	.8	2.4	2.8	.7	.4	2.73
Santa Ana	1964	25	.1	.1	.1	.2	.2	.3	.3	.8	1.5	3.9	8.4	1.3	.5	3.82
Santa Barbara	1964	25	.2	.3	.3	.4	.4	.5	.7	1.2	2.1	3.4	5.0	1.1	.7	2.52
Dist. of Col.																
Washington	1964	26	.1	.1	.1	.2	.3	.5	1.1	1.5	2.0	2.9	6.2	1.3	.6	3.85
Georgia																
Atlanta	1964	26			.1	.1	.1	.1	.2	.2	.2	.3	.6	.2	.2	1.80

(continued)

APPENDIX

TABLE 17

CONCENTRATIONS OF AMMONIUM IN AIR, UNITED STATES (Continued)

Location	Year	No. of Samp.	Min	Micrograms Per Cubic Meter — Frequency Distribution-Percent									Max	Arith Mean	Geom Mean	Std Geom Dev
				10	20	30	40	50	60	70	80	90				
Hawaii																
Honolulu	1964	26						.1	.1	.1	.1	.1	.2	.1	.1	1.48
Illinois																
Moline	1964	24	.1		.1	.1	.1	.2	.2	.2	.2	.3	1.3	.2	.2	1.80
Peoria	1964	23	.4	.4	.6	.7	.8	1.0	1.2	1.4	1.5	3.4	5.8	1.4	1.1	2.02
Rock Island	1964	25	.1	.2	.3	.3	.3	.4	.5	.7	.8	.9	1.5	.5	.5	1.79
Indiana																
Evansville	1964	23	.1	.1	.3	.4	.5	.7	1.1	1.7	2.7	4.0	12.7	1.9	.9	3.52
Fort Wayne	1964	25	.1	.2	.2	.3	.3	.4	.5	.7	1.1	1.0	3.4	.7	.5	2.30
Muncie	1963	25	.1	.1	.1	.2	.2	.3	.7	.0	1.1	2.3	6.5	.9	.5	3.06
South Bend	1963	26	.1	.1	.1	.1	.2	.3	.7	1.3	3.4	7.5	10.8	2.0	.6	6.99
Terre Haute	1963	24	.1	.1	.2	.3	.4	.9	1.1	1.8	3.4	7.5	9.6	2.3	1.0	4.02
Iowa																
Dubuque	1964	26	.1	.2	.2	.3	.3	.5	.6	.7	1.1	1.5	6.4	.9	.6	2.42
Kansas																
Kansas City	1964	25	.1		.1	.1	.1	.2	.2	.3	.3	.5	1.7	.3	.2	2.09
Kentucky																
Ashland	1964	24	.2	.2	1.1	2.4	3.2	5.0	6.4	11.2	19.4	43.2	75.5	12.7	4.5	5.70
Covington	1964	24	.2	.1	.2	.2	.4	.8	1.0	1.3	1.8	2.4	4.8	1.1	.7	2.77
Louisville	1964	21	.1	.1	.2	.3	.5	.6	.8	1.5	2.4	3.9	7.9	1.5	.8	3.32
Louisiana																
Baton Rouge	1964	26	.1			.1	.1	.1	.2	.2	.3	.4	.7	.2	.2	1.87
Maryland																
Cumberland	1963	26	.1	.1	.1	.1	.2	.2	.3	.5	.7	1.8	6.1	.8	.3	3.21

(continued)

APPENDIX

TABLE 17

CONCENTRATIONS OF AMMONIUM IN AIR, UNITED STATES (Continued)

Location	Year	No. of Samp.	Min	Micrograms Per Cubic Meter Frequency Distribution-Percent 10	20	30	40	50	60	70	80	90	Max	Arith Mean	Geom Mean	Std Geom Dev
Michigan																
Flint	1963	23	.1	.1	.1	.1	.1	.2	.2	.2	.3	.4	.5	.2	.2	1.61
Grand Rapids	1963	24	.1		.1	.1	.1	.2	.2	.2	.3	.4	1.1	.2	.2	1.84
Muskegon	1963	26	.1	.1	.1	.1	.1	.2	.2	.2	.3	.6	1.2	.3	.2	1.94
Minnesota																
Minneapolis	1964	26	.1			.1	.1	.1	.2	.2	.3	.3	1.0	.2	.2	1.91
St. Paul	1964	26	.1		.1	.2	.2	.3	.4	.7	.8	1.4	4.7	.7	.4	2.93
Missouri																
Kansas City	1964	25	.3	.3	.3	.4	.4	.5	.5	.6	.6	.6	.9	.5	.5	1.35
Nevada																
Reno	1963	24	.1		.1	.1	.2	.3	.5	.6	.9	1.8	4.7	.7	.4	2.94
New Jersey																
Bayonne	1963	24	.1	.1	.2	.6	1.4	2.1	2.7	4.9	5.4	8.8	12.4	3.4	1.6	4.49
Camden	1964	26	.1	.2	.5	.8	2.0	3.4	5.4	6.4	7.5	10.9	17.5	4.7	2.2	4.56
Jersey City	1963	25	.2	.2	.5	1.1	1.8	3.4	4.9	5.3	6.4	7.5	13.4	3.8	2.1	3.65
New Mexico																
Albuquerque	1964	26	.1	.1	.1	.2	.2	.2	.4	.5	.5	.6	2.6	.4	.3	2.21
North Carolina																
Charlotte	1964	25	.2	.2	.2	.3	.3	.3	.4	.5	1.4	2.4	3.8	.8	.5	2.46

(continued)

APPENDIX

TABLE 17

CONCENTRATIONS OF AMMONIUM IN AIR, UNITED STATES (Continued)

Location	Year	No. of Samp.	Micrograms Per Cubic Meter													Std Geom Dev
			Min	Frequency Distribution-Percent									Max	Arith Mean	Geom Mean	
				10	20	30	40	50	60	70	80	90				
Ohio																
Columbus	1964	26	.1	.1	.1	.2	.2	.4	.5	.6	.7	.9	1.4	.5	.4	2.07
Dayton	1964	26	.1	.1	.1	.2	.2	.2	.3	.5	.7	1.3	4.1	.6	.4	2.42
Lorain	1964	25	.1	.1	.1	.2	.2	.3	.3	.5	.8	2.9	10.0	1.1	.4	3.31
Stuebenville	1964	24	.1	.1	.6	.9	1.5	1.8	2.0	2.7	3.4	6.4	10.2	2.5	1.5	3.38
Youngstown	1964	25	.1	.1	.2	.3	.4	.5	.6	1.0	1.5	2.1	8.8	1.2	.6	3.19
Pennsylvania																
Altoona	1963	22	.1	.1	.2	.3	.4	.6	1.1	1.8	5.9	6.4	13.7	2.5	.9	4.35
Puerto Rico																
Guayanilla	1964	26	.1			.1	.1	.1	.1	.2	.2	.2	.3	.2	.2	1.53
Texas																
Houston	1964	24	.2	.1	.2	.2	.2	.3	.3	.3	.4	.4	.5	.3	.3	1.41
Utah																
Salt Lake City	1964	24	.1			.1	.1	.1	.2	.3	.5	1.5	1.9	.4	.2	2.78
West Virginia																
Huntington	1964	24	.1	.1	.2	.2	.3	.4	.5	.8	1.3	5.4	11.5	1.5	.6	3.41
Wisconsin																
Milwaukee	1964	26	.1			.1	.1	.1	.1	.2	.3	.5	.9	.2	.2	2.06
Wyoming																
Cheyenne	1964	23	.1					.1	.1	.1	.1	.1	.1	.1	.1	1.02